

CHAPTER XXX

METALLURGY OF BERYLLIUM

Source: Metallurgiya legkikh Metallov, Metallurgizdat,  
pp 523-531 (Ch. XXX).

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SECTION III  
METALLURGY OF OTHER LIGHT METALS

CHAPTER 30

METALLURGY OF BERYLLIUM

110. Properties of Beryllium and its Uses

Despite the fact that free metallic beryllium was isolated shortly after the separation of aluminum (in 1828), its technical application is rather recent, due to the numerous difficulties in developing industrial methods of beryllium production.

While the chemical properties of beryllium are similar to those of other light metals, its physical and mechanical properties exhibit several peculiarities (table 84).

PROPERTIES OF BERYLLIUM

CHARACTERISTIC FEATURES	MAGNITUDE
Atomic weight	9.02
Valence	2
Specific gravity at 20 degrees Centigrade	1.85
Melting point, degrees Centigrade	1200
Heat of fusion, calories per gram	341
Hardness coefficient (Mohs)	6-7
Electrical conductivity relative to copper, (in percent)	8.3
Contact potential relative to hydrogen, volts	-0.81
Electro-chemical equivalent, grams per ampere hour	0.168

Beryllium's low specific gravity of 1.85 makes it  $1/3$  <sup>lighter?</sup> (as light as) <sup>2.7 times</sup> ~~aluminum~~ <sup>aluminum</sup>. Having great hardness and fragility, beryllium is rated from 6-7 on Mohs scale of hardness, and at ordinary temperatures the metal scratches glass. Beryllium is so brittle that the blow of a hammer cracks it; therefore, pure beryllium cannot be rolled, drawn nor forged. At elevated temperatures (purple heat), a certain degree of

beryllium malleability is observed, permitting the stamping of small laminae. Some plasticity is exhibited by very pure vacuum-produced beryllium.

The melting point of beryllium (1280 degrees Centigrade) is considerably higher than that of other light metals, almost twice that of aluminum or magnesium. Of all the metals, beryllium has the highest heat of fusion, equal to 341 calories per gram. The boiling point of beryllium has not been yet accurately determined.

At the melting point the vapor pressure of beryllium is negligible. Beryllium's volatility becomes noticeable at temperatures in excess of 1,500 degrees. The electrical conductivity of beryllium is equal to 1/12 that of copper. A remarkable property of beryllium is its high permeability to X-rays; 17 times that of aluminum. This property of beryllium accounts for successful use in X-ray tubes.

Chemically, beryllium is very similar to aluminum. Like aluminum, beryllium is highly soluble in acids and alkali, and has a strong affinity to oxygen. However, due to a film of surface oxide, beryllium, again like aluminum, is very stable at ordinary air temperatures relative to atmospheric oxygen. At high temperatures (in excess of 1200 degrees) beryllium becomes an active deoxidizer and reduces such stable oxides as  $Al_2O_3$ ,  $BaO$ ,  $MgO$ , etc.

Its unfavorable physical properties prevent any appreciable use of pure beryllium. The metal's most important use is as a component of cuproberyllium alloys containing 1-3 percent of Be (so-called beryllium bronzes, the hardness and durability of which exceed those of all known non-ferrous alloys). For example, the 2.5 percent cuproberyllium alloy has a hardness of from 80 to 100 (Brinell) and tensile strength of 48-50 Kilograms per square Centimeter. Heat treating the alloy increases its hardness to 350-370 (Brinell) and the corresponding tensile strength to 120-150 Kilograms per square Millimeter.

Chemically, the cuproberyllium alloys are similar to the aluminum bronzes; they are stable in air, in sea water, and do not oxidize readily

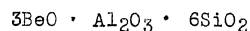
when heated. Due to their high tensile strength, elasticity and negligible fatigue when subjected to prolonged bending, the cuproberyllium alloys are widely used for all kinds of springs. Their high electrical conductivity makes them highly appropriate for manufacturing springy parts of electrical apparatus (relays, meters, etc.). Finally, the considerable heat conductivity of the beryllium bronzes renders them especially suitable as parts in internal combustion engines.

Admixtures of beryllium have a similar effect on the properties of ferrous metals (iron, nickel, cobalt and chromium).

Due to its strong affinity for oxygen, beryllium is also used as a deoxidizing agent in foundries. For example, a trace of beryllium, say a few hundredths of one percent, suffices to reduce copper completely. As a deoxidizer, beryllium is usually used in the form of a cuprous alloy containing 10 percent beryllium. This alloy is introduced into the mass of copper which is to be deoxidized prior to founding. Traces of beryllium with light aluminum and magnesium alloys, greatly raise their anti-corrosion stability.

#### 111. Raw Materials Used for Beryllium

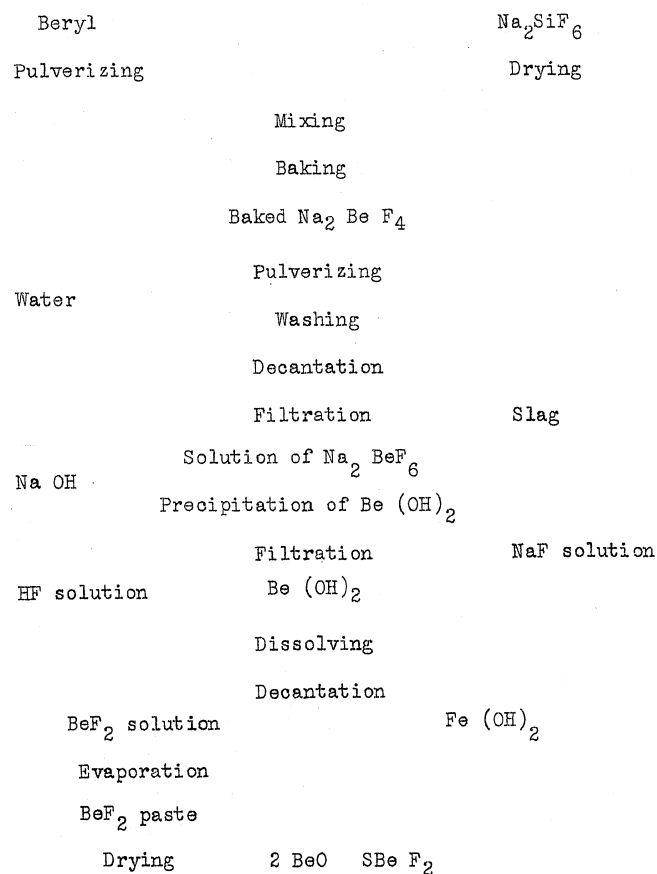
Beryllium is present in a number of minerals. The earth crust contains a 0.0001 percent of beryllium by weight. However, for practical purposes, only one mineral, beryl, which gave beryllium its name, is important. Beryl is an aluminum silicate of beryllium with the following chemical composition:



containing 3.6 percent of beryllium. In its purest form as a green emerald, tinted by chromic oxide, beryl was well known in ancient times and valued as a precious stone. Metallic beryllium is extracted from common beryl which is found in considerable quantities in various countries. The most important beryl deposits are in Spain (province of Pontevedra), Brazil, Canada, United States and the USSR. In the USSR the most important beryl deposits are in the Urals around the city of Sverdlovsk (Emerald mines), around the city of Zlatoust in the southern Urals (in the Sinarka region).

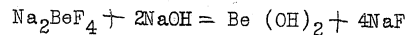
There are known beryl deposits in Eastern Siberia (<sup>h</sup>Scherlo<sup>va</sup> mountain) and in the Altai; beryl is also found in the quartz galleries of Lake Ilmen.

The basic material for the extraction of metallic beryllium is its salt - beryllium oxyfluoride -  $2 \text{ BeO} \cdot 5 \text{ BeF}$  which is obtained from beryl. The flow sheet of the beryllium oxyfluoride extraction process from beryl is given in figure 207 below.

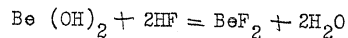


[27] Figure 207. Technological flow for obtaining beryllium oxyfluoride

Finely pulverized beryl is mixed with an equal amount of dried sodium fluosilicate ( $\text{Na}_2 \text{Si F}_6$ ) and the mixture is baked at 700-750 degrees, the result being a porous aggregate, containing  $\text{Na}_2 \text{Be F}_4$ . This aggregate is further leached with water at 80-90 degrees. The solution after washing and decantation is filtered and pumped over into a precipitation tank provided with a mixer. A 20 percent solution of  $\text{Na OH}$  is introduced into this tank which precipitates beryllium hydroxide.



Beryllium hydroxide is filtered from the sodium fluoride solution, washed, dried and subsequently treated in a lead tank with a 30 percent solution of hydrofluoric acid to obtain beryllium fluoride:



Simultaneously, an admixture of iron hydroxide is precipitated out of the beryllium hydroxide and is deposited on the bottom of the tank.

$\text{BeF}_2$  solution, free of iron is then decanted into a lead-lined container where it is evaporated until it reaches a paste-like consistency.

Beryllium fluoride paste is then dried at a temperature of 250 degrees with the resultant partial formation of  $\text{BeO}$  and  $\text{HF}$  due to hydrolytic dissociation. Beryllium oxyfluoride -  $2\text{BeO} \cdot 5\text{BeF}_2$  is the principal result of this drying, and represents the basic source of metallic beryllium. The following are the weight proportions, expressed in tons, of the various components to produce 1 ton of beryllium fluoride: beryl (containing 10 percent of  $\text{BeO}$ )-9.0; sodium fluosilicate (96 percent)-9.3; caustic (40 percent)-1.5; hydrofluoric acid (40 percent)-1.5.

#### 112. Technological Production of Metallic Beryllium

Metallic beryllium was first obtained by F. Wohler in 1828 by reducing beryllium chloride with metallic potassium. In the process Wohler used a platinum crucible inside of which he placed beryllium chloride interlaid with flattened pieces of potassium. The crucible was then tightly covered and heated. After cooling, the contents of the crucible were leached with water, and beryllium obtained in the form of a blackish-gray powder, which

was then washed and dried. Subsequent attempts at beryllium extraction also involved methods of chemical reduction. However, as in the case of aluminum, the only profitable method of obtaining pure beryllium is through electrolysis of molten substances. The first successful electrolytic process for the production of metallic beryllium was that of Lebeau, who in 1898 electrolyzed molten double fluorides of sodium and beryllium -  $\text{NaBeF}_3$  and  $\text{Na}_2\text{BeF}_4$ . These compounds produce a clear liquid-mass, having good electrical conductivity. The electrolysis of these compounds was performed in a nickel crucible, which simultaneously served as the cathode. Anodes were made of carbon. Upon the completion of electrolysis, the cooled electrolyte was pulverized and leached with water. The metallic beryllium produced was in the form of a fibrous mass, easily separated from the crucible walls. This took place because the process could be conducted at a temperature of 600-750 degrees, which is below the melting point of beryllium.

At higher temperatures there is a tendency on the part of the double fluorides to volatilize. Beryllium, <sup>thus produced in the solid state, was obtained,</sup> ~~output this obtained was now due to~~ <sup>due to large losses in the electrolyte, with very low current consumption.</sup> ~~large losses of electrolyte.~~

Beryllium electrolysis at higher than melting point temperature (1280 degrees) was first performed in 1920 by Shtok, Goldschmidt and Priss, who utilized a mixture of  $\text{BaBeF}_4$  and  $\text{BaBe}_2\text{F}_6$ , having negligible volatilization in the 1300-1400 degrees temperature range.

As a result of this, metallic beryllium could be obtained in the compact molten state.

A crytolite furnace is used to heat a coal graphite crucible which at the same time serves as anode. A hollow water-cooled iron post serves as the cathode, and is immersed a few millimeters in the molten mass. Electrolysis is then conducted at 60 ampere and 20 volts with periodic additions of  $\text{BaBeF}_4$ . Due to the high specific gravity of the electrolyte, beryllium floats to the surface and is deposited at the cathode as a rounded ingot. In this way it was possible to obtain beryllium in a compact manner. However, this did not assure a continuous process, since the electrolyte

gradually became saturated with barium and required periodic replenishment.

This process of Shtok and Goldschmidt was considerably improved, and now, known as the <sup>Siemens-Halske</sup> Simens-Galske process, is used to produce pure beryllium.

The Simens-Galske process is continuous and uses  $\text{BaF}_2$  and  $5\text{BeF}_2 \cdot 2\text{BeO}$  as the electrolytic molten mass, wherein the latter compound is alone expendable and constantly replenished in the electrolytic process.

Figure 208 (General appearance of the Simens-Galske Electrolyzer for Producing Metallic Beryllium)., shows the general appearance of and Figure 209 (Schematic diagram of the Simens-Galske Electrolyzer for Producing Metallic Beryllium), depicts the scheme of the apparatus used for electrolyzing the beryllium oxyfluoride.

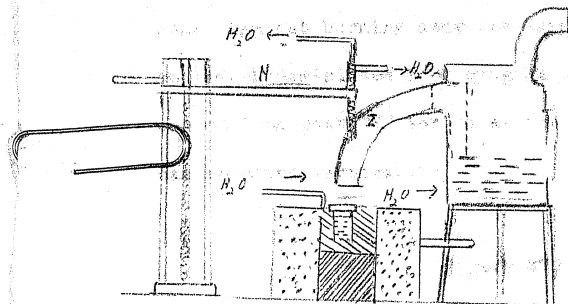


Figure 208 (General appearance of the Simens-Galske Electrolyzer for the production of metallic beryllium.)

Vapors produced in the course of the electrolysis, as well as the gaseous anode-deposited carbon compound ( $\text{CF}_4$ ) are conducted via pipe into a water-circulating absorption tower, wherein the  $\text{BaBeF}_4$  is precipitated out as a powder, and the  $2\text{BeO} \cdot 5\text{BeF}_2$  is dissolved in water. The  $\text{CF}_4$  compound undergoes hydrolytic dissociation which produces  $\text{HF}$ , soluble in water. Thus, it is possible to recover up to 90 percent of the evaporating fluoride and reuse it in the process.

To start the electrolyser, a mixture of freely melting  $\text{NaF}$  and  $2\text{BeO} \cdot 5\text{BeF}_2$  is introduced, and as the operation progresses and the temperature



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Figure 209

Figure 209 (Schematic diagram of the Simens-Galske electrolyzer for the production of metallic beryllium.)

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risers, a mixture of  $\text{BaF}_2$  and  $2\text{BeO} \cdot 5\text{BeF}_2$  is introduced into the crucible. As the temperature reaches 1400 degrees, beryllium starts to deposit on the cathode, which just touches the surface of the electrolyte. Beryllium hardens at the cathode post, which is gradually, so that the beryllium is stretched out in the shape of a post of non-uniform cross-section. Such posts of beryllium could be 50 Centimeters long and 10 Centimeters in diameter. The  $2\text{BeO} \cdot 5\text{BeF}_2$  is periodically added to the electrolyte. The output of beryllium is primarily dependent on the relative proportions of  $2\text{BeO} \cdot 5\text{BeF}_2$  and  $\text{BaF}_2$  in the electrolyte. The most favorable proportion is 1:1 for which beryllium output for a given current reaches 75-80 percent (Figure 210).

Beryllium Output versus Relative  
Content of  $2\text{BeO} \cdot 5\text{BeF}_2$  and  $\text{BaF}_2$   
in the Electrolyte.

The graphite crucible, which also serves as the anode, undergoes gradual deterioration, due to  $\text{F}_2$  and  $\text{O}_2$  deposits, and must be periodically replaced.

The Siemens-Galske electrolyzers operate at 55 volts and 600 amperes. When pure salt compounds are used, the metallic beryllium is usually 99.5 percent pure, the most important admixtures being iron (0.3 percent), aluminum (0.1 percent) and carbon (0.04 percent).

Since beryllium is mainly used in heavy metal alloys (copper, nickel and iron), electrolytic production of beryllium alloys is of interest. For this purpose, powdered heavy metal to be alloyed with beryllium, is periodically introduced into a Siemens-Galske installation. The metallic powder settles on the floor of the crucible, which acts as the anode, and there under the influence of liberated fluorine, the metal is transformed into a corresponding fluoride, which, together with beryllium, is deposited at the cathode. Thus alloys containing 18-20 percent of heavy metal are produced, which possess certain advantages compared with pure beryllium

(ease of smelting, negligible loss in burning, etc.).

Alloys, having a small beryllium content, can also be produced by thermal treatment, by reduction of melted beryllium salts with active metals (magnesium, for example), in the presence of melted copper or other heavy metal.

For this purpose there is prepared a corresponding cupromagnesium or a cupronickel alloy which is crucible-melted together with sodium fluoro-beryllate ( $\text{NaBeF}_3$  or  $\text{Na}_2\text{BeF}_4$ ) under a layer of table salt which acts as a fusing agent. Magnesium displaces beryllium from the fluoroberyllate, which in turn forms a required alloy with copper or nickel. Alumino-beryllium alloys can be obtained in a similar way. At present, cuproberyllium and cupronickel alloys are obtained in considerable quantities through the reduction of beryllium oxide by carbon in an electric furnace. This process is conducted with considerable amounts of copper or nickel at a temperature of about 2,000 degrees. These alloys are used as admixtures in the preparation of beryllium alloys <sup>1,2</sup>.

1. Stott LL Steel, 1941, 27, X vol. 17, 109

2. Chem. Age. 1942, vol. LVIII, No. 1205, 112.

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